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Exploiting σ/π Coordination Isomerism to Prepare Homologous Organoalkali Metal (Li, Na, K) Monomers with Identical Ligand Sets

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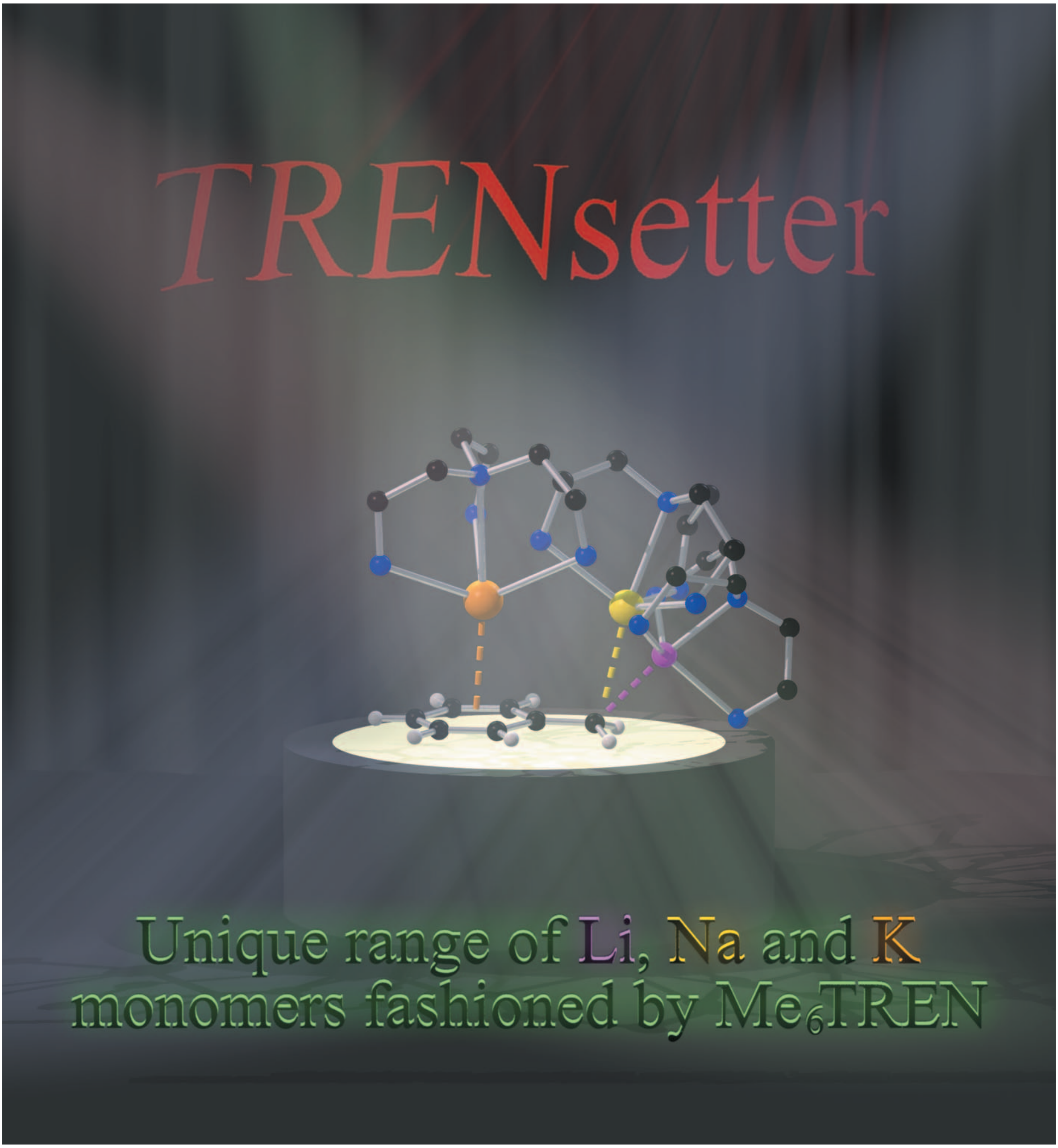

Abstract: Tetraamine Me_6TREN has been used as a scaffold support to provide coordinative saturation in the complexes $PhCH_2M{\cdot}Me_6TREN$ (M = Li, Na, K). The Li derivative displays a Li−C σ interaction with a pyramidalized CH_2 both in the solid state and in solution, and represents the first example of η^4 coordination of Me_6TREN to lithium. In the sodium derivative, the metal cation slips slightly towards the delocalized π electrons whilst maintaining a partial σ interaction with the CH_2 group. For the potassium case, coordinative saturation successfully yields the first monomeric benzylpotassium complex, in which the anion binds to the metal cation exclusively through its delocalized π system resulting in a planar CH_2 group.

Keywords: alkali metals · benzyl anion · coordination isomerism · monomer · polyamines

Long indispensable to synthetic practitioners of chemistry, simple organolithium (and increasingly organo alkali metal) compounds have a rich, diverse structural chemistry.[1] In solution, where these compounds are routinely employed as reagents,[2] multiple species involving aggregration and/or solvation as well as assorted dynamic processes can be in existence,[3] making structure–reactivity correlation extremely complex and difficult to untangle. Such complexes, of general formula $[RM]_x{\cdot}nL$, can adopt a prodigious variety of chain or cyclic structures falling between the two extremes of monomer ($x=1$) and polymer ($x=\infty$), with the degree of aggregation generally being inversely proportional to the reactivity.[4] The factors governing the extent of aggregation include the identity of the cation (M) and the anion (R), the presence or absence of a neutral Lewis donating ligand (L), the degree of ligation (n) and the size and denticity of R and L. Given this number of influential components, it is clear that changing just one variable can have a profound effect on the others and thus on the final structure. This is eloquently illustrated by *n*-butyl- and *tert*-butyllithium; on changing from the linear to the more bulky branched alkyl group, Stalke and Kottke showed that the solid-state structure of the unsolvated derivatives alters from a hexamer ($x=6$) to a tetramer ($x=4$).[5] Further, the introduction of a Lewis donor to the latter complex ($L=Et_2O$) invokes a decrease in aggregation yielding a dimer $[t\mathrm{BuLi}{\cdot}Et_2O]_2$.[5] A fine example of variable reactivity was unveiled by Mitzel and co-workers who demonstrated that *n*BuLi and *t*BuLi deprotonate 1,3,5-trimethyl-1,3,5-triazacyclohexane (TMTAC) at the doubly deactivated aminal (NCH_2N) position,[6] while the same ligand acts only as a donor[7] to polymeric MeLi.[8] The influence of complex to donor ratio (i.e. n) was exposed most recently by a pair of structures $[n\mathrm{BuLi}{\cdot}\mathrm{TMCDA}]_2$ and $[n\mathrm{BuLi}{\cdot}\mathrm{TMCDA}]_2[n\mathrm{BuLi}]_2$ (TMCDA = *N,N,N′,N′*-tetramethylcyclohexane-1,2-diamine) from varying such ratio.[9] Of course it is not prudent to surmise that larger anions or larger polydentate donors will automatically result in smaller aggregates since electronic factors will also play an important role. While lithium complexes are often smaller (and consequently more soluble) oligomers, heavier sodium and potassium derivatives have a tendency to give larger insoluble polymers; for example, hexameric $LiCH_2SiMe_3$[10] is commercially available as a hexane solution yet its K congener is insoluble in the same medium.[11] Whereas judicious choice of anion and Lewis donor can disrupt the polymerization of lithium species, it is much more arduous to do so with Na or K complexes of simple organic anions.[12] As a consequence of this there is a paucity of successful structural studies pertaining to simple organopotassium complexes in the literature. This general dichotomy between Li and K chemistry is principally due to the fundamental differences between these two monocations—among them, lithium has a considerably greater charge density, forms σ bonds to carbanionic species, and can only accommodate a small number of neutral Lewis donors around it; whereas potassium is softer, more polarizable, has a larger coordination sphere and possesses a considerable affinity for π-electron density.[13] The behavior of sodium can be considered intermediate between these two and can fall into either category. Consequently these differences encountered as one navigates Group 1 means, to the best of our knowledge, there are no known crystallographically characterized isomeric molecular organo alkali-metal species in the literature.[14] To that end, we were interested in the challenge of preparing a family of *isomeric* Lewis donor stabilized *monomers* (i.e., homologues which only varied in M), which required careful consideration over the component parts. As reported herein, this challenge has now been unequivocally met to reveal facets of the fundamental structure and bonding proclivities of Li, Na, and K summarized above.

The potential to coordinate via a σ or π interaction made the benzyl ($PhCH_2^-$) anion appear attractive for such a quest. While $PhCH_2Li$ has been shown to exist as a monomer in the presence of either the tridentate cyclic donor *N,N′,N″*-trimethyl-1,4,7-triazacyclononane (Me_3TACN)[15] or the mixed donor system *N,N,N′,N′*-tetramethyl-1,2-ethylenediamine/tetrahydrofuran (TMEDA/THF),[16] the real chal-

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lenge would be to prevent polymerization of the sodium[17] and potassium derivative by effecting coordinative saturation.[18] Due to its versatile ($\eta^{3[19]}$ or $\eta^{4[20]}$) denticity, and recent application in Group 1 metal chemistry,[19c] tris(*N,N*-dimethyl-2-aminoethyl)amine (Me_6TREN)[21] seemed a logical choice of donor as it could act as a protective scaffold, covering but not completely encapsulating a range of alkali metals thus leaving space for coordination of the anion. Synthetically, this was achieved by adding the tetraamine to a colorless solution of LiTMP (TMP = 2,2,6,6-tetramethylpiperidide) in toluene. The activating presence of the heteroatomic additive induced metallation[22] of the solvent, which was evident via an immediate color change to yellow/orange. Slow evaporation of the solvent yielded a crop of orange crystals of $PhCH_2Li{\cdot}Me_6TREN$ (**1**), which were subjected to a single-crystal X-ray diffraction study.[23]

The solid-state structure (Figure 1, pertinent bond parameters are presented in Table 1) shows that complex **1** consists of discrete monomeric units as seen previously in $PhCH_2Li{\cdot}Me_3TACN$ but with the lithium center in an unusual five-coordinate (trigonal-bipyramidal) environment, with such coordinative saturation preventing polymerization. This represents the first example of η^4 coordination of Me_6TREN to a lithium cation, presumably facilitated by the lack of steric bulk at the anionic moiety.[24] The structure contains a Li–C σ bond and importantly shows no significant interactions between the metal and the phenyl ring, in contrast to the mixed solvate $PhCH_2Li{\cdot}TMEDA{\cdot}THF$,[16] which has a considerably tighter C-C-Li angle [94.6(2)°] and shorter Li–C_{ipso} [2.722(5) Å] and Li–C_{ortho} [3.366(6) and 3.486(6) Å] distances. The -$CH_2CH_2NMe_2$ arms are inequivalent in the solid state due to the nonlinearity at C20 with the aromatic ring displaced towards N2 and N3 and away from N1. The Li–N distances lie in the range 2.162(3)–2.356(3) Å with the average (2.250 Å) noticeably greater than that in $PhCH_2Li{\cdot}TACN$ (2.10 Å),[15] $PhCH_2Li{\cdot}TMEDA{\cdot}THF$ (2.148 Å)[16] and $PhCH_2Li{\cdot}DABCO$ (2.10 Å, DABCO = 1,4-diazabicyclo[2.2.2]octane),[25] which can be attributed to the greater number of Lewis donors per cation in **1**.

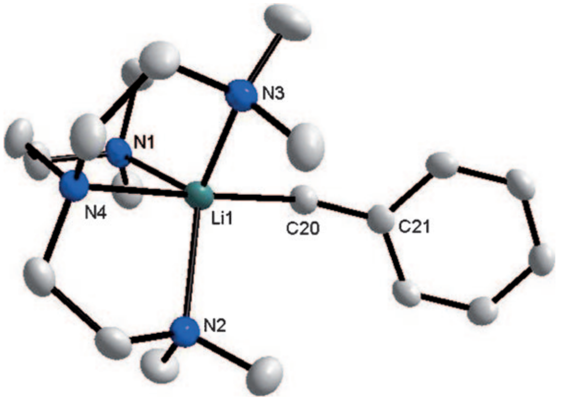

Figure 1. Molecular structure of one of the independent molecules of **1** with hydrogen atoms and toluene of crystallization omitted and thermal ellipsoids drawn at 50 % probability.

Table 1. Selected bond parameters of complexes **1**–**3** (values for second independent molecule of **1** are in brackets).

	1	**2**	**3**
M–C_α [Å]	2.352(3) [2.335(3)]	2.556(1)	3.893(4)
M–C_{ipso} [Å]	3.467(3) [3.362(3)]	3.183(1)	3.098(4)
M–C_{ipso}/M–C_α	1.47 [1.44]	1.24	0.80
C_α–C_{ipso} [Å]	1.400(3) [1.400(2)]	1.397(2)	1.390(6)
M-C_α-C_{ipso} [°]	133.4(2) [126.4(1)]	103.3(1)	46.2(2)
C_{ortho}-C_{ipso}-C_{ortho} [°]	113.4(2) [113.4(1)]	113.4(1)	113.6(4)

For the heavier metal derivatives, addition of Me_6TREN to a toluene suspension of $PhCH_2M$ (M = Na, K, prepared via a superbasic *t*BuOM/*n*BuLi mixture[26]) resulted in a homogeneous red solution. Slow diffusion of hexane into this toluene solution at 5 °C yielded a crop of red crystals of $PhCH_2Na{\cdot}Me_6TREN$ (**2**); cooling the toluene solution to −35 °C was sufficient to yield a large crop of red crystals of $PhCH_2K{\cdot}Me_6TREN$ (**3**). Elucidated by X-ray crystallography, the molecular structure of **2** is displayed in Figure 2.[23]

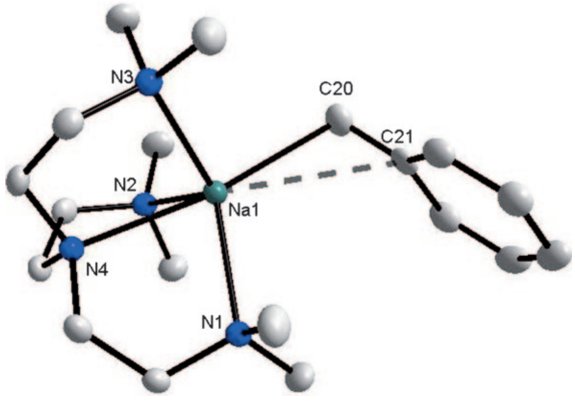

Figure 2. Molecular structure of **2** with hydrogen atoms and toluene of crystallization omitted and thermal ellipsoids drawn at 50 % probability.

Like **1**, the molecular structure of **2** is monomeric with a five-coordinate trigonal-bipyramidal metal center, representing the first crystallographically characterized monomeric benzylsodium complex.[27] The principal difference however, is that although the sodium cation appears to be σ-bonded to the 'carbanionic' center, it has, together with its polyamine scaffold, started to migrate towards the aromatic ring. This is clearly evidenced by the much less obtuse angle at C20 [103.3(1)°], which brings the metal into much closer proximity of the *ipso*-carbon atom. Indeed, while comparing absolute bond lengths with **1** is futile due to the presence of different alkali metals, comparing the ratios of the M–C_{ipso}:M–C_α bond lengths is revealing. This value is 1.47 in **1** (1.44 for the second independent molecule) but is reduced to 1.24 in **2**, clearly demonstrating the movement of the alkali metal to a position where M–π-bonding interactions may play a role. Again, nonlinearity at C20 forces the phenyl ring towards one of the arms of the ligand (N1) making these three pendant groups inequivalent.

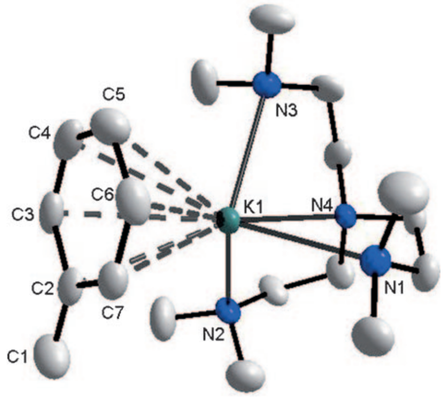

Figure 3. Molecular structure of one of the independent molecules of **3** with hydrogen atoms omitted and thermal ellipsoids drawn at 50 % probability. K···C π-arene contacts are denoted by dashed lines.

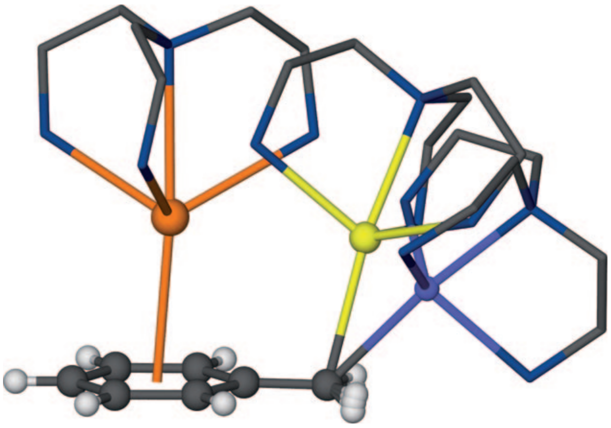

Figure 4. Superimposition of solid-state structures of **1** (purple), **2** (yellow), and **3** (orange) with methyl carbon atoms and all protons omitted from the Me_6TREN molecule for clarity.

The molecular structure of **3**[23] (Figure 3) was also experimentally determined and revealed the presence of two independent molecules, one was disordered over the benzyl anion and the Me_6TREN molecule, however the other showed no disorder whatsoever.

Mimicking **1** and **2**, the Me_6TREN ligand in **3** ligates to the cation in a η^4 manner via its four nitrogen lone pairs, with the coordinative saturation successfully preventing polymerization such as that previously found for the PMDETA-[28] or THF-solvated[29] derivatives of benzylpotassium. Remarkably, the potassium cation shows no interaction with the CH_2 arm [$K\cdots C_\alpha$ separation distance = 3.893(4) Å] but rather has slipped round accompanied by its multidentate Lewis donor scaffold to bind exclusively to the delocalized π system of the aromatic ring [3.097(4)–3.250(4) Å, av 3.156 Å] resulting in a naked CH_2 head. While K–π interactions of this nature are precedented due to the affinity of potassium for adopting multihapto environments,[30] this structure represents, to the best of our knowledge, the first example of a benzylpotassium complex free of a cation–C_α interaction. For example, $[PhCH_2K\cdot PMDETA]_\infty$ shows η^3 coordination to the carbanionic [3.171(2) Å], *ipso*-carbon [3.218(2) Å] and one *ortho*-carbon [3.297(2) Å].[28] The bulkier triaryl-substituted $Ph_3CK\cdot PMDETA\cdot THF$ shows no $K{-}C_\alpha$ interaction but this may also be due to extensive electron delocalization promoted by the presence of two other aromatic rings.[13b] The potassium center of **3** lies in a distorted trigonal-bipyramidal environment with the center of the benzyl π system [K···centroid distance = 2.8234(7) Å] and N4 in the axial positions and N1–N3 in the equatorial positions. For a more complete list of bond parameters of complexes **1**–**3** see the Supporting Information. The slippage of the Me_6TREN-protected metal cation is clearly illustrated in Figure 4, which shows a superimposition of the three structures with the benzyl anion kept in a constant position.

A structural consequence of this movement by the alkali metal away from the CH_2 group and towards the aromatic π system is a deformation of the C_6 ring due to delocalization of the negative charge on C_α into the aryl ring. Delocalization is generally negated by the charge localizing influence of a highly charged cation, which is in close proximity to C_α (i.e., as in **1**) and is favored by larger cations (i.e., as in **3**). Such ring deformations have been comprehensively and eloquently described by Harder and co-workers.[30a,b,31] In particular, delocalized structures should display shortened $C_\alpha{-}C_{ipso}$ and $C_{ortho}{-}C_{meta}$ bonds along with elongated $C_{ipso}{-}C_{ortho}$ and $C_{meta}{-}C_{para}$ bonds. This consequently influences bond angles, giving C_{ipso} and C_{para} angles smaller than the expected value of 120° and larger angles at C_{ortho} and C_{meta}. Such deformation clearly takes place in complexes **1**–**3** (Figure 5) with the greater degree of deformation, and thus charge delocalization, occurring in **3** as expected due to the lesser proximity of the metal to C_α in accord with the NMR data (vide infra).

NMR spectral data suggest the structures of **1**–**3** are maintained in solution, with appropriate resonances for the aromatic, carbanionic, and ligand groups all accounted for (Table 2). Despite the inequivalence of the $\text{-}CH_2CH_2NMe_2$ arms in the solid state (vide supra), each environment is equivalent in solution due to free rotation around the M–C bond; indeed the two Me_6TREN CH_2 environments in **2** are completely indistinguishable by ^1H NMR spectroscopy.

Table 2. NMR resonances of starting materials and complexes **1**, **2**, and **3** (all values in ppm).

	C_7H_8/Me_6TREN		**1**		**2**		**3**	
	^1H	^{13}C	^1H	^{13}C	^1H	^{13}C	^1H	^{13}C
para	7.05	125.6	6.23	105.7	5.93	101.1	5.24	94.1
meta	7.13	128.5	7.08	128.8	6.93	129.8	6.56	130.4
ortho	7.02	129.3	6.76	117.6	6.57	114.0	6.16	111.3
ipso	–	137.8	–	161.3	–	158.4	–	153.0
CH_2^-	2.12[a]	21.4[a]	2.08	37.8	2.51	41.2	3.21	56.2
CH_2 (TREN)	2.40	54.0	1.86	51.3	1.78	50.8	2.02	52.3
CH_2 (TREN)	2.66	58.7	1.97	57.3	1.78	57.0	2.08	57.4
CH_3 (TREN)	2.14	46.0	2.00	45.5	2.00	45.1	2.04	45.1

[a] CH_3.

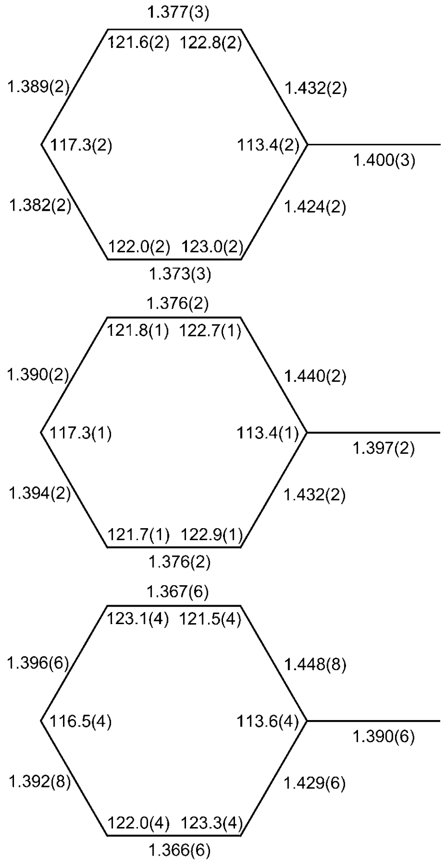

Figure 5. Bond parameters (in Å and °) for the benzyl anion of **1** (top), **2** (middle), and **3** (bottom). The parameters of the second independent molecule of **1** are within experimental error of those given and have thus been omitted for clarity.

NMR data, in particular $^1J(^{13}C–^1H)$ coupling constants, can be utilized to predict the amount of delocalization through the benzyl anion.[30b,32] The $^1J(^{13}C–^1H)$ coupling constant is extremely sensitive to the hybridization of the deprotonated carbon atom. A pyramidalized (sp^3) benzyl carbanion is expected to show such a coupling constant of 125 Hz, while the expected value for a planar (sp^2) CH_2^- group is 167 Hz.[16] Complex **1** displayed a coupling constant at the sp^3 end of the scale (132 Hz), suggesting a pyramidalized C_α in solution, consistent with the solid-state structure, while that of complex **3** was 151 Hz[33] clearly more towards the planar end of the scale. The value for **2** was 142 Hz, intermediate between the Li and K values.

The chemical shift of the *para* C–H is also highly indicative of charge delocalization,[31] since as the metal migrates away from the CH_2 group and towards the aromatic ring, the interaction between the metal and the aromatic system increases. This is clearly the case in this series as Table 2 shows, with a considerable upfield shift occurring for the *para* C and H resonances on going from **1** to **3**.

In summary, we have successfully used the tetraamine Me_6TREN as a scaffold support to provide coordinative saturation in the congeneric complexes $PhCH_2M{\cdot}Me_6TREN$ (M = Li, Na, K). The first product displays a Li–C σ interaction with a pyramidalized CH_2 group both in the solid state and in solution and represents the first example of η^4 coordination of Me_6TREN to lithium. Moving to sodium, the metal cation slips slightly towards the delocalized π electrons whilst maintaining a partial σ interaction with the CH_2 group. Coordinative saturation successfully yields the first monomeric benzylpotassium complex which, to the best of our knowledge, is the smallest molecular weight molecular organo-potassium compound ever to be characterized crystallographically.[34] The anion binds to the metal cation exclusively through its delocalized π system resulting in a planar CH_2 group. This begs the question, "is the principal interaction in polymers of type $PhCH_2K{\cdot}$donor actually the π interaction with polymerization facilitated via a secondary σ interaction rather than the other way round as conventionally thought?" We now intend to investigate if these monomers display increased reactivity with respect to their oligomeric counterparts.

Experimental Section

All reactions were carried out under a protective argon atmosphere using standard Schlenk techniques. Full details, including complete characterization, are given in the Supporting Information.

Synthesis of $PhCH_2Li{\cdot}Me_6TREN$ (1): LiTMP (0.294 g, 2 mmol) was dissolved in toluene (10 mL) and Me_6TREN (0.53 mL, 2 mmol) was added by using a syringe with stirring to yield an orange solution. This was dried in vacuo to give an oily product. Fresh toluene (5 mL) was added and this was removed very slowly under reduced pressure until a crop of orange crystals slowly precipitated (0.395 g, 53 %).

Synthesis of $PhCH_2Na{\cdot}Me_6TREN$ (2): $PhCH_2Na$ (0.114 g, 1 mmol) was weighed into a clean dry Schlenk flask and suspended in toluene (8 mL). Me_6TREN was added dropwise until a homogeneous orange solution resulted (0.26 mL, 1 mmol). Slow diffusion of hexane into this solution at 5 °C yielded a crop of red crystals (0.104 g, 30 %).

Synthesis of $PhCH_2K{\cdot}Me_6TREN$ (3): $PhCH_2K$ (0.130 g, 1 mmol) was weighed into a clean dry Schlenk flask and suspended in toluene (8 mL). Me_6TREN was added dropwise until a homogeneous orange solution resulted (0.53 mL, 2 mmol). This solution was cooled to −30 °C overnight to yield a crop of red crystals (0.236 g, 64 %).

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[23] Crystal data for **1**: $\mathrm{C_{20.75}H_{39}LiN_4}$; an orange plate gave the triclinic space group $P\bar{1}$, $a=9.2836(3)$, $b=14.3353(5)$, $c=17.4903(6)$ Å, $\alpha=97.155(3)$, $\beta=103.094(3)$, $\gamma=93.311(3)°$, $V=2240.6(1)$ Å^3, $T=123(2)$ K, $Z=4$, $\rho_{\mathrm{calcd}}=1.042\ \mathrm{Mg\,m^{-3}}$, $\mathrm{Mo_{K\alpha}}$ $\lambda==0.71073$ Å, $R1=0.0460$ (for 5414 reflections with $I>2s(I)$) $wR2=0.1104$ and $S=0.890$ for 507 parameters and 9771 independent reflections. Min/Max residual electron density 0.284/−0.207 e Å^{-3}. Crystal data for **2**: $\mathrm{C_{26}H_{45}NaN_4}$; a red plate gave the orthorhombic space group $P2_12_12_1$, $a=9.3986(3)$, $b=14.8466(5)$, $c=19.2843(6)$ Å, $V=2690.9(1)$ Å^3, $T=123(2)$ K, $Z=4$, $\rho_{\mathrm{calcd}}=1.078\ \mathrm{Mg\,m^{-3}}$, $\mathrm{Mo_{K\alpha}}$ $\lambda=0.71073$ Å, $R1=0.0318$ (for 5413 reflections with $I>2s(I)$) $wR2=0.0682$ and $S=0.950$ for 294 parameters and 6582 independent reflections. Min/Max residual electron density 0.167/−0.183 e Å^{-3}. Crystal data for **3**: $\mathrm{C_{19}H_{37}KN_4}$; a red plate gave the monoclinic space group $P2_1/c$, $a=15.8222(5)$, $b=18.4801(4)$, $c=16.1656(5)$ Å, $\beta=109.962(4)°$, $V=4442.7(2)$ Å^3, $T=123(2)$ K, $Z=8$, $\rho_{\mathrm{calcd}}=1.078\ \mathrm{Mg\,m^{-3}}$, $\mathrm{Mo_{K\alpha}}$ $\lambda=0.71073$ Å, $R1=0.0735$ (for 5210 reflections with $I>2s(I)$) $wR2=0.2145$ and $S=1.050$ for 425 parameters and 8719 independent reflections. Min/Max residual electron density 0.888/−0.495 e Å^{-3}. CCDC-790265 (**1**), CCDC-790266 (**2**), and CCDC-790267 (**3**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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[34] A search of the Cambridge Crystallographic Database[27] suggests that organopotassium complexes require either a bulky anion or a bulky donor to force formation of a monomer. The lowest molecular weight example reported thus far seems to be CpK·[18]crown-6 ($M_{\mathrm{W}}=368.51$ amu): S. Neander, F. E. Tio, R. Buschmann, U. Behrens, F. Olbrich, *J. Organomet. Chem.* **1999**, *582*, 58.

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